Effects of chromophore concentration and film thickness on thermo-optic properties of electro-optic fluorinated polyimide films

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Electro-optic (EO) effect and thermo-optic (TO) effect are jointly considered on the basis of field-induced and temperature-affected perturbations of the operating point in waveguide components. TO coefficients of EO fluorinated polyimide films with side-chain azobenzene chromophore were measured by attenuated-total-reflection (ATR) technique at different temperatures with TE- and TM-polarized lights, respectively. It is found that the absolute values of TO coefficients increase with the increments of both chromophore concentration and film thickness, but the polarization dependence of TO coefficients increases with the increment of chromophore concentration and decreases with the increment of film thickness.

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Nonlinear optical (NLO) polymeric materials have recently attracted great attention for their potential applications in optical communication devices[1−5]. Because the values of thermo-optic (TO) coefficients (i.e. the temperature-dependent change in refractive index, $\mathrm{d}n/\mathrm{d}T$) are generally larger than those of inorganic materials by one order of magnitude, TO effect is frequently utilized for dynamic control of refractive index n in operating waveguide components[6]. Hence, the investigation of controlling TO properties by electro-optic (EO) materials selves is an essential issue to reduce the field-induced and temperature-affected perturbations[7−10].

According to Prod'homme's theory[11], the values of $\mathrm{d}n/\mathrm{d}T$ for polymeric materials can be expressed by the derivative of Lorentz-Lorenz equation[11]:

$$\frac{\mathrm{d}n}{\mathrm{d}T} = -\eta\beta, \tag{1}$$

with

$$\eta = \frac{\left(n^2-1\right)\left(n^2+2\right)}{6n}, \tag{2}$$

where β is the coefficient of thermal volume expansion.

Recently, the values of $\mathrm{d}n/\mathrm{d}T$ for polyimide (PI) have been obtained in a digit range of 10^{-5} to 10^{-3}[7]. However, the $\mathrm{d}n/\mathrm{d}T$ values and their polarization dependence $\mathrm{d}(\Delta n)/\mathrm{d}T$ for EO PI films are less studied. In this paper, the effects of chromophore concentration and film thickness on the TO properties of EO fluorinated PI films with side-chain azobenzene chromophore (SFPI) are investigated.

The SFPI films were prepared by spin-coating on the bases of grass prisms evaporated by a silver silm of thickness of 50 nm and thermal imidization of their precursors, poly(amic acid) (PAA) were condensed from 4,4'-prime-(hexafluoroisopropylidene) diphthalic arhydride (6FDA) and m-phenylene diamine (MPD), and then post-azo-coupled with azobenzene chromophore[12]. Another layer of 100-nm-thick silver film was evaporated onto SFPIs surface as an optical coupling layer. Their chemical structures are shown in Fig. 1.

The chromophore concentration in SFPI was measured by an ultraviolet-visible (UV-VIS) spectrum in solvent of N-methyl-pyrrolidone (NMP). The refractive indices n and thicknesses h were measured in an attenuated-total-reflection (ATR) setup equipped with an auto temperature-control apparatus[12] with TE- and TM-polarized light at 1064 nm, respectively. In order to reduce the hygroscopic influence, the measurement temperatures declined from 80 to 20 °C with the interval of 20 °C.

As shown in Fig. 2, a collimated light beam from a diode laser passes through a polarizer and is then incident upon the interface between the prism and the silver film

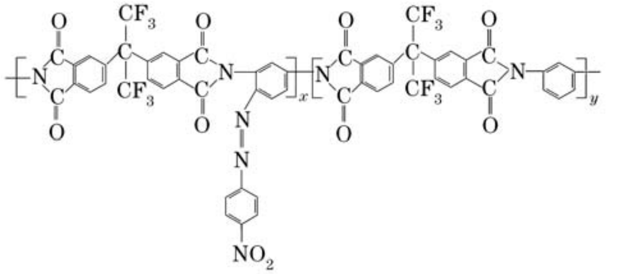

Fig. 1. Chemical structures of SFPI, x and y are the molar percentages of chain units with or without chromophore.

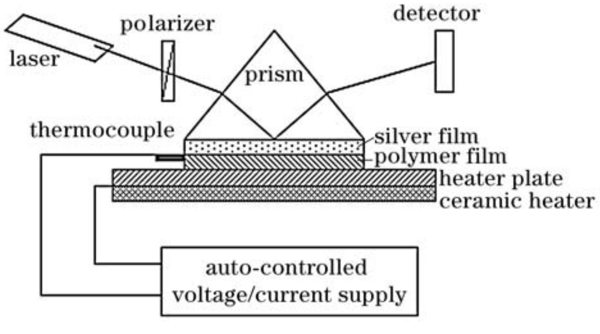

Fig. 2. Prism coupler device with auto-controlled heat stage.

Table 1. Thermo-Optic Properties of SFPI Films

C (wt.-%)	n_{av}	Δn	η_{av}	$\Delta\eta$	β_{av} ($\times10^{-4}$)	$\Delta\beta$ ($\times10^{-4}$)	$\mathrm{d}n_{\mathrm{av}}/\mathrm{d}T$ ($\times10^{-4}$ K^{-1})	$\mathrm{d}(\Delta n)/\mathrm{d}T$ ($\times10^{-4}$ K^{-1})
0	1.5469	0.0098	0.6593	0.0147	1.23	0.29	−0.81	−0.21
12.6	1.5586	0.0102	0.6769	0.0155	3.84	0.35	−2.60	−0.29
21.5	1.5667	0.0107	0.6893	0.0163	4.34	0.38	−2.99	−0.33
22.4	1.5675	0.0111	0.6905	0.017	4.39	0.40	−3.03	−0.35
22.8	1.5679	0.0108	0.6911	0.0165	4.40	0.41	−3.04	−0.36

C: concentration; $n_{\mathrm{av}}^2 = (n_{\mathrm{TE}}^2 - n_{\mathrm{TM}}^2)/2$, $\Delta n = n_{\mathrm{TE}} - n_{\mathrm{TM}}$, $\Delta\beta = \beta_{\mathrm{TE}} - \beta_{\mathrm{TM}}$, $\mathrm{d}(\Delta n)/\mathrm{d}T = \mathrm{d}n_{\mathrm{TE}}/\mathrm{d}T - \mathrm{d}n_{\mathrm{TM}}/\mathrm{d}T$.

with an appropriate angle. An angular scan is carried out by a $\theta/2$ computer-controlled goniometer. Reflected light is detected with a photodiode by averaging output signal. In the experiment, the goniometer keeps rotating to generate the ATR spectrum on the computer screen, a series of dips in reflectivity due to resonant transfer of energy into guide modes can be clearly observed. Variation of refractive index with temperature can be determined through the angle shift of the resonant dips.

As shown in Table 1, the absolute values of all film parameters of SFPI increase with the increment of chromophore concentration. The TE mode in flat waveguide has larger influence on n and β than TM mode out of flat waveguide, because the flat waveguide is nearly clamped by two silver films and aromatic rings orient in plane. According to Eqs. (1) and (2), large $\mathrm{d}n_{\mathrm{av}}/\mathrm{d}T$ is achieved for higher n_{av} and higher β_{av}. The effects of chromophore concentration on η_{av} and β_{av} for SFPI films are shown in Fig. 3.

The values of β_{av} increase more quickly than those of η_{av} with the increment of chromophore concentration. It indicates that chromophore concentration has larger influence on β_{av} than on n_{av}. According to the molar refraction[13], the introduction of azobenzene will improve the value of n. But the increment of side-chain has greater influence on the reduction of interaction of backbone chains and the enlargement of polymer's free volumes. Until the chromophore concentration goes beyond 20 wt.-%, the increment of β gets slow due to effect of cis-trans isomerization of the nitrogen benzene groups[13]. The weak parabolic curve feature of side chain type polymeric systems is different from that of host-guest polymeric systems due to the linkage of azobenzene chromophore in backbone chains[11].

The effect of chromophore concentration on $\mathrm{d}n/\mathrm{d}T$ and $\mathrm{d}(\Delta n)/\mathrm{d}T$ is shown in Fig. 4. Orientation in SFPI films is normally affected by spin-coating. The SFPI films with azobenzene chromophore were clamped in two silver films and cooled to below their glass transition temperature before the molecules have a chance to relax to their random coiled configuration. Anisotropy means that SFPI films have different properties in different directions. Birefringence is evidenced by the ability of a material to rotate the plane of polarized light. Nitrogen in side chain improves the optical sensitivity function, hence the stress-optical coefficient ($C\sigma$) increases and birefringence is enhanced.

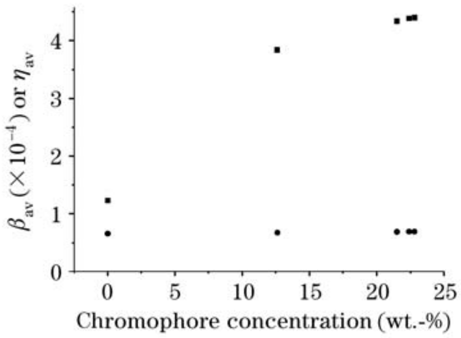

Fig. 3. Effects of chromophore concentration on η_{av} (dots) and β_{av} (squares).

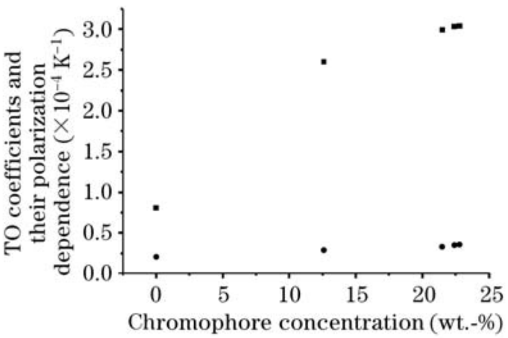

Fig. 4. Effects of chromophore concentration on $|\mathrm{d}n_{\mathrm{av}}/\mathrm{d}T|$ (squares) and $|\mathrm{d}(\Delta n)/\mathrm{d}T|$ (dots) of SFPI films.

Furthermore, the values of β of SFPIs with different chromophore concentration in TE- and TM-polarization are very different for the clamping of film in two silver films. From

$$\mathrm{d}(\Delta n)/\mathrm{d}T \approx -\eta_{\mathrm{av}}\left(\beta_{\mathrm{TE}} - \beta_{\mathrm{TM}}\right), \tag{3}$$

β_{TE} is generally larger than β_{TM}, and the difference between β_{TE} and β_{TM} is getting larger as the increment of chromophore concentration.

The SFPI films are nearly clamped in the in-plane direction and are free to expand normal to the film plane due to a linear thermal expansion[14]. According to

$$\frac{\mathrm{d}n}{\mathrm{d}T} = -\eta\beta \propto -\eta a_{\mathrm{l}}^3 = \frac{-\eta}{l^3}\left(\frac{\mathrm{d}l}{\mathrm{d}T}\right)^3, \tag{4}$$

where a_{l} is the coefficient of linear thermal expansion. The value of $\mathrm{d}n/\mathrm{d}T$ decreases with the increment of film thickness h (i.e. l in TM polarization) when the value of η is set. The effects of film thickness on $|\mathrm{d}n_{\mathrm{av}}/\mathrm{d}T|$ and $|\mathrm{d}(\Delta n)/\mathrm{d}T|$ are shown in Fig. 5.

The value of $|\mathrm{d}n_{\mathrm{av}}/\mathrm{d}T|$ increases and the value of $|\mathrm{d}(\Delta n)/\mathrm{d}T|$ decreases with the increment of film thickness. The value of $\mathrm{d}n/\mathrm{d}T$ depends on the density via the linear thermal expansion coefficient a_{l}. According

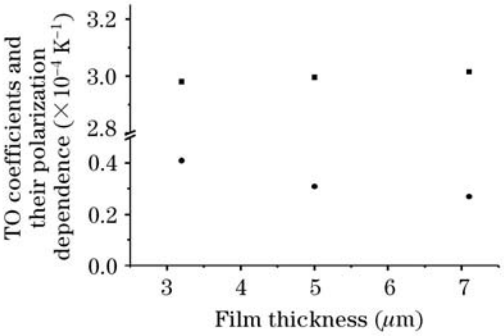

Fig. 5. Effects of film thickness on $|\mathrm{d}n_{\mathrm{av}}/\mathrm{d}T|$ (squares) and $|\mathrm{d}(\Delta n)/\mathrm{d}T|$ (dots) with chromophore concentration of 22.8 wt.-%.

to polymer physics theory, the density in bulk is generally larger than that in surface. Hence, the density of SFPI films increases with the increment of thickness. Furthermore, along with the increment of film thickness, the films change to bulk and their anisotropy effect gets weak. As a result, the density in TM polarization increases obviously particularly. These changes induce the weak increment of refractive indices and reduction of polarization sensitivity.

In conclusion, the SFPI films exhibit large TO coefficients and polarization dependence due to the introduction of side-chain azobenzene chromophore. The NLO coefficients, TO coefficients and their polarization dependence of EO PI can be improved by controlling chromophore concentration and film thickness.

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